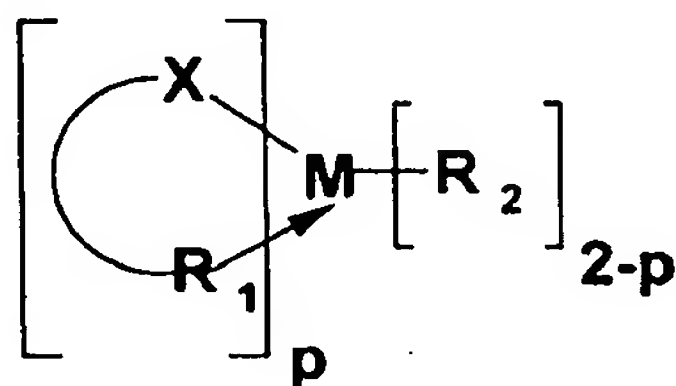


Claims

- [1] A method of producing cyclic olefin polymers having polar functional groups, the method comprising:
 preparing a catalyst mixture including
 i) a procatalyst represented by formula (1) containing a group 10 metal and a ligand containing hetero atoms bonded to the metal;
 ii) a cocatalyst represented by formula (2) including a salt compound which is capable of providing a phosphonium cation and an anion weakly coordinating to the metal of the procatalyst; and
 addition-polymerizing cyclic olefin monomers having polar functional groups in the presence of an organic solvent and the catalyst mixture, at a temperature of 80-150 °C :



(1)

where X is a hetero atom selected from S, O and N;

R_1 is -CH=CHR²⁰, -OR²⁰, -SR²⁰, -N(R²⁰)₂, -N=NR²⁰, -P(R²⁰)₂, -C(O)R²⁰, -C(R²⁰)=NR²⁰, -C(O)OR²⁰, -OC(O)OR²⁰, -OC(O)R²⁰, -C(R²⁰)=CHC(O)R²⁰, -R²¹C(O)R²⁰, -R²¹C(O)OR²⁰ or -R²¹OC(O)R²⁰, in which R²⁰ is a hydrogen, a halogen, a linear or branched C₁₋₅ alkyl, a linear or branched C₁₋₅ haloalkyl, a linear or branched C₅₋₁₀ cycloalkyl, a linear or branched C₂₋₅ alkenyl, a linear or branched C₂₋₅ haloalkenyl, or an optionally substituted C₇₋₂₄ aralkyl, and R²¹ is a C₁₋₂₀ hydrocarbylene;

R_2 is a linear or branched C₁₋₂₀ alkyl, alkenyl or vinyl; a C₅₋₁₂ cycloalkyl optionally substituted by a hydrocarbon; a C₆₋₄₀ aryl optionally substituted by a hydrocarbon; a C₇₋₁₅ aralkyl optionally substituted by a hydrocarbon; or C₃₋₂₀ alkynyl;

M is a Group 10 metal; and

p is an integer from 0 to 2, and

$[(R_3)_3-P(R_4)_a(R_4')_b[Z(R_5)_d]_c][Ani]$ (2)

where each of a, b and c is an integer from 0 to 3, and a+b+c = 3;

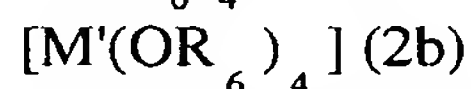
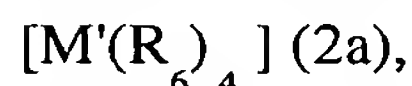
Z is O, S, Si or N;

d is 1 when Z is O or S, d is 2 when Z is N, and d is 3 when Z is Si;

R_3 is a hydrogen, an alkyl, or an aryl;

each of R_4 , R_4' and R_5 is a hydrogen; a linear or branched C_{1-20} alkyl, alkoxy, allyl, alkenyl or vinyl; a C_{3-12} cycloalkyl optionally substituted by a hydrocarbon; a C_{6-40} aryl optionally substituted by a hydrocarbon; a C_{7-15} aralkyl optionally substituted by a hydrocarbon; a C_{3-20} alkynyl; a tri(linear or branched C_{1-10} alkyl)silyl; a tri(linear or branched C_{1-10} alkoxy)silyl; a tri(optionally substituted C_{3-12} cycloalkyl)silyl; a tri(optionally substituted C_{6-40} aryl)silyl; a tri(optionally substituted C_{6-40} aryloxy)silyl; a tri(linear or branched C_{1-10} alkyl)siloxy; a tri(optionally substituted C_{3-12} cycloalkyl)siloxy; or a tri(optionally substituted C_{6-40} aryl)siloxy, in which each substituent is a halogen or C_{1-20} haloalkyl; and [Ani] is an anion capable of weakly coordinating to the metal M of the procatalyst represented by formula (1) and is selected from the group consisting of borate, aluminate, $[SbF_6]^-$, $[PF_6]^-$, $[AsF_6]^-$, perfluoroacetate($[CF_3CO_2]^-$), perfluoropropionate($[C_2F_5CO_2]^-$), perfluorobutyrate($[CF_3CF_2CF_2CO_2]^-$), perchlorate($[ClO_4]^-$), p-toluenesulfonate($[p-CH_3C_6H_4SO_3]^-$), $[SO_3CF_3]^-$, boratabenzene, and carborane optionally substituted with a halogen.

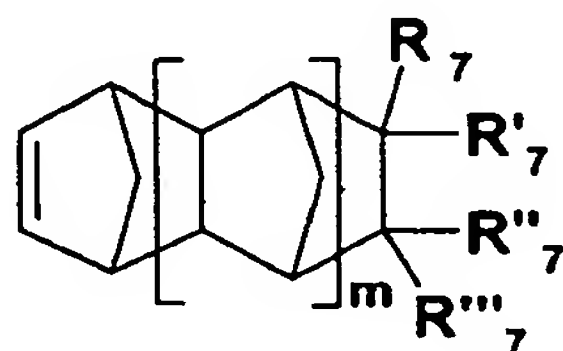
[2] The method of claim 1, wherein the borate or aluminate of formula (2) is an anion represented by formula (2a) or (2b):



where M' is B or Al;

R_6 is each independently a halogen, a linear or branched C_{1-20} alkyl or alkenyl optionally substituted by a halogen, a C_{3-12} cycloalkyl optionally substituted by a halogen, a C_{6-40} aryl optionally substituted by a hydrocarbon, a C_{6-40} aryl optionally substituted by a linear or branched C_{3-20} trialkylsiloxy or a linear or branched C_{18-48} triarylsiloxy, or a C_{7-15} aralkyl optionally substituted by a halogen.

[3] The method of claim 1, wherein the cyclic olefin monomer is a compound represented by formula (3):

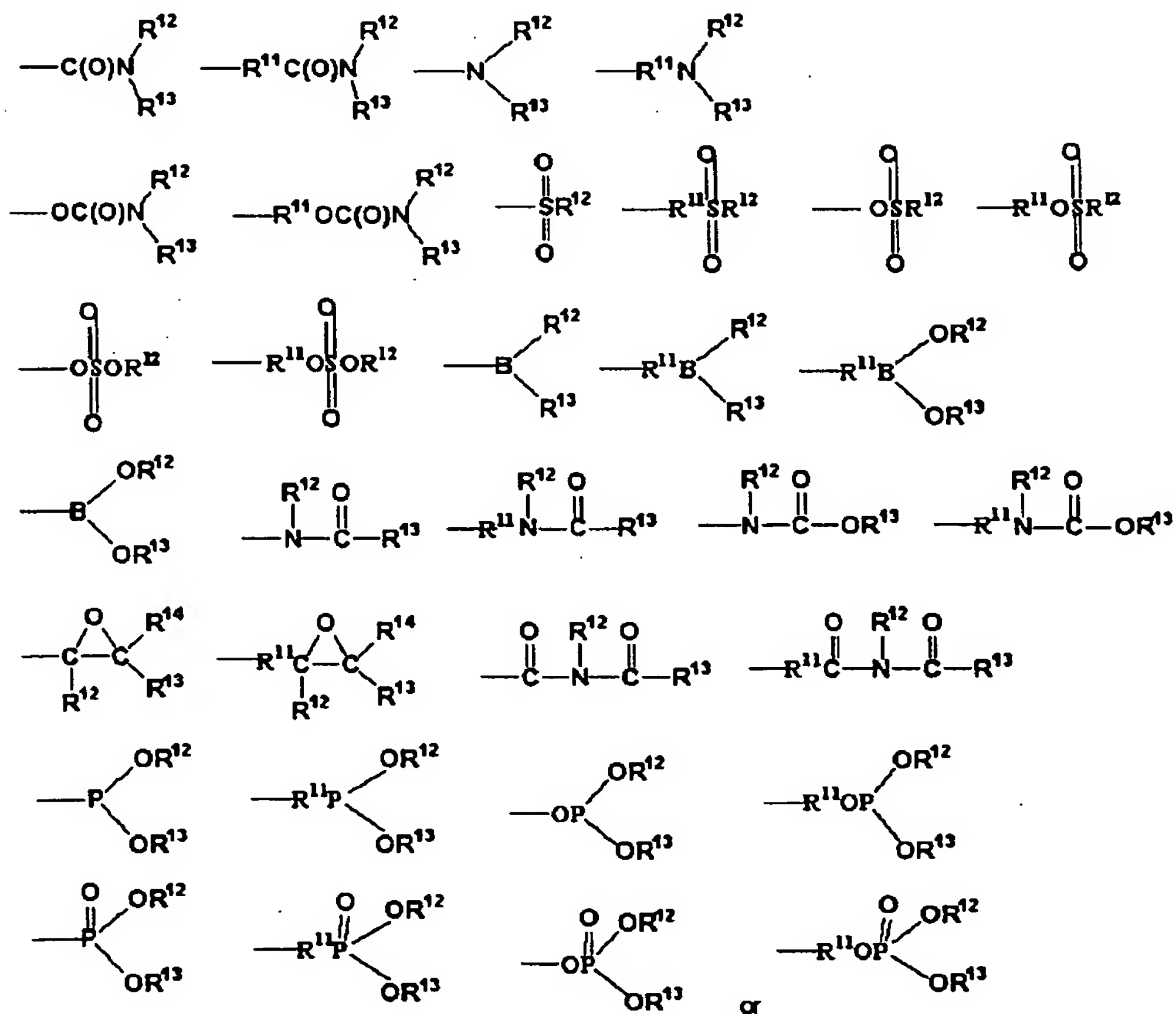


(3)

where m is an integer from 0 to 4;

at least one of R_7 , R_7' , R_7'' and R_7''' is a polar functional group and the others are nonpolar functional groups;

R_7 , R_7' , R_7'' and R_7''' can be bonded together to form a saturated or unsaturated C_{4-12} cyclic group or a C_{6-24} aromatic ring;
 the nonpolar functional group is a hydrogen; a halogen; a linear or branched C_{1-20} alkyl, haloalkyl, alkenyl or haloalkenyl; a linear or branched C_{3-20} alkynyl or haloalkynyl; a C_{3-12} cycloalkyl optionally substituted by an alkyl, an alkenyl, an alkynyl, a halogen, a haloalkyl, a haloalkenyl or haloalkynyl; a C_{6-40} aryl optionally substituted by an alkyl, an alkenyl, an alkynyl, a halogen, a haloalkyl, a haloalkenyl or haloalkynyl; or a C_{7-15} aralkyl optionally substituted by an alkyl, an alkenyl, an alkynyl, a halogen, a haloalkyl, a haloalkenyl or haloalkynyl;
 the polar functional group is a non-hydrocarbonaceous polar group having at least one O, N, P, S, Si or B and is $-R^8OR^9$, $-OR^9$, $-OC(O)OR^9$, $-R^8OC(O)OR^9$, $-C(O)R^9$, $-R^8C(O)OR^9$, $-C(O)OR^9$, $-R^8C(O)R^9$, $-OC(O)R^9$, $-R^8OC(O)R^9$, $-(R^8O)-OR^9$, $-(OR^8)-OR^9$, $-C(O)-O-C(O)R^9$, $-R^8C(O)-O-C(O)R^9$, $-SR^9$, $-R^8SR^9$, $-SSR^8$, $-R^8SSR^9$, $-S(=O)R^9$, $-R^8S(=O)R^9$, $-R^8C(=S)R^9$, $-R^8C(=S)SR^9$, $-R^8SO_3R^9$, $-SO_3R^9$, $-R^8N=C=S$, $-NCO$, R^8-NCO , $-CN$, $-R^8CN$, $-NNC(=S)R^9$, $-R^8NNC(=S)R^9$, $-NO_2$, $-R^8NO_2$,

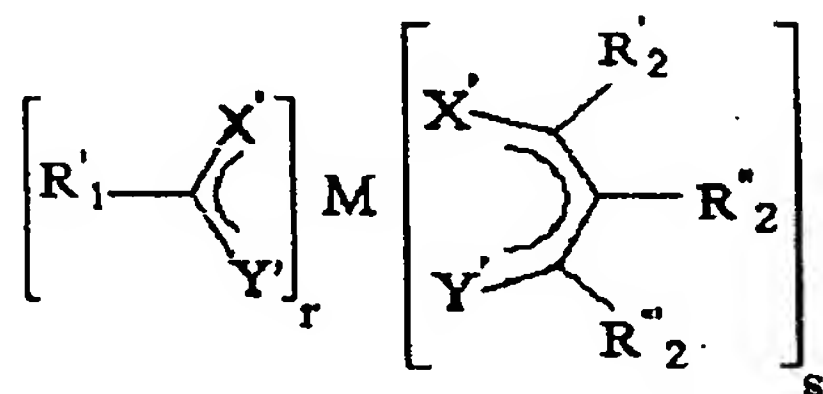


in which each of R^8 and R^{11} is a linear or branched C_{1-20} alkylene, haloalkylene, alkenylene or haloalkenylene; a linear or branched C_{3-20} alkynylene or haloalkynylene; a C_{3-12} cycloalkylene optionally substituted by an alkyl, an alkenyl, an alkynyl, a halogen, a haloalkyl, a haloalkenyl or haloalkynyl; a C_{6-40} arylene optionally substituted by an alkyl, an alkenyl, an alkynyl, a halogen, a haloalkyl, a haloalkenyl or haloalkynyl; or a C_{7-15} aralkylene optionally substituted by an alkyl, an alkenyl, an alkynyl, a halogen, a haloalkyl, a haloalkenyl or haloalkynyl;

each of R^9 , R^{10} , R^{12} and R^{13} is a hydrogen; a halogen; a linear or branched C_{1-20} alkyl, haloalkyl, alkenyl or haloalkenyl; a linear or branched C_{3-20} alkynyl or haloalkynyl; a C_{3-12} cycloalkyl optionally substituted by an alkyl, an alkenyl, an alkynyl, a halogen, a haloalkyl, a haloalkenyl or haloalkynyl; a C_{6-40} aryl optionally substituted by an alkyl, an alkenyl, an alkynyl, a halogen, a haloalkyl, a haloalkenyl or haloalkynyl; a C_{7-15} aralkyl optionally substituted by an alkyl, an alkenyl, an alkynyl, a halogen, a haloalkyl, a haloalkenyl or haloalkynyl; or an alkoxy, an haloalkoxy, a carbonyloxy or a halocarbonyloxy; and

k is an integer from 1 to 10.

- [4] The method of claim 1, wherein the procatalyst represented by formula (1) and the cocatalyst represented by formula (2) are a palladium compound represented by formula (4) and a phosphonium compound represented by formula (5), respectively;



(4)

where each of X' and Y' is a hetero atom selected from S and O;

each of R_1' , R_2' , R_2'' and R_2''' is a linear or branched C_{1-20} alkyl, alkenyl or vinyl; a C_{5-12} cycloalkyl optionally substituted by a hydrocarbon; a C_{6-40} aryl optionally substituted by a hydrocarbon; a C_{7-15} aralkyl optionally substituted by a hydrocarbon; or a C_{3-20} alkynyl;

M is a Group 10 metal; and

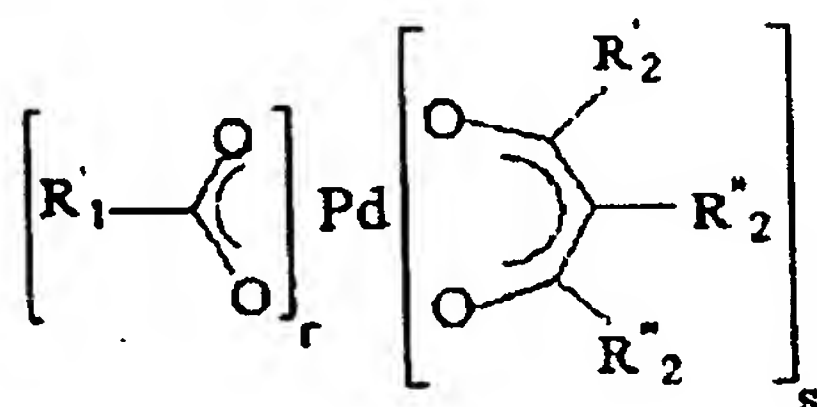
each of r and s is an integer from 0 to 2 and $r+s = 2$, and

$[H-P(R_4)_3][Ani]$ (5)

where R_4 is a hydrogen; a linear or branched C_{1-20} alkyl, alkoxy, allyl, alkenyl or vinyl; an optionally substituted C_{3-12} cycloalkyl; an optionally substituted C_{6-40}

aryl; an optionally substituted C_{7-15} aralkyl; or a C_{3-20} alkynyl, in which each substituent is a halogen or a C_{1-20} haloalkyl; and [Ani] is an anion capable of weakly coordinating to the metal M of the procatalyst represented by formula (1) and is selected from the group consisting of borate, aluminate, $[SbF_6]^-$, $[PF_6]^-$, $[AsF_6]^-$, perfluoroacetate($[CF_3CO_2]^-$), perfluoropropionate($[C_2F_5CO_2]^-$), perfluorobutyrate($[CF_3CF_2CF_2CO_2]^-$), perchlorate($[ClO_4]^-$), p-toluenesulfonate($[p-CH_3C_6H_4SO_3]^-$), $[SO_3CF_3]^-$, boratabenzene, and carborane optionally substituted by a halogen.

- [5] The method of claim 1, wherein the procatalyst represented by formula (1) and the cocatalyst represented by formula (2) are a palladium compound represented by formula (4a) and a phosphonium compound represented by formula (5), respectively;



(4a)

where each of R_1' , R_2' , R_2'' and R_2''' is a linear or branched C_{1-20} alkyl, alkenyl or vinyl; a C_{5-12} cycloalkyl optionally substituted by a hydrocarbon; a C_{6-40} aryl optionally substituted by a hydrocarbon; a C_{7-15} aralkyl optionally substituted by a hydrocarbon; or a C_{3-20} alkynyl; and each of r and s is an integer from 0 to 2 and $r+s=2$, and

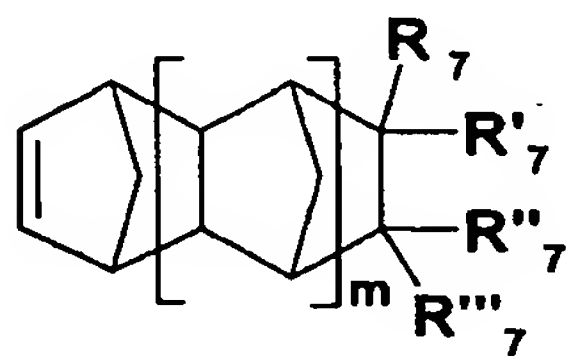
$[H-P(R_4)_3][Ani]$ (5)

where R_4 and [Ani] are as defined in claim 4.

- [6] The method of claims 1, wherein in the procatalyst represented by formula (1), the metal is Pd, p is 2, and the ligand having a hetero atom directly coordinating to the metal is acetylacetonate or acetate, and in the cocatalyst including a salt compound having phosphonium represented by formula (2), b is 0, c is 0, R_3 is H, and R_4 is cyclohexyl, isopropyl, t-butyl, n-butyl or ethyl.
- [7] The method of claim 1, wherein a molar ratio of the cocatalyst to the procatalyst is 0.5-10:1.
- [8] The method of claim 1, wherein the catalyst mixture is supported on an inorganic support.
- [9] The method of claim 8, wherein the inorganic support is at least one selected from the group consisting of silica, titania, silica/chromia, silica/chromia/titania, silica/alumina, aluminum phosphate gel, silanized silica, silica hydrogel, mont-

morillonite clay and zeolite.

- [10] The method of claim 1, wherein an organic solvent used to dissolve the catalyst mixture is at least one solvent selected from the group consisting of dichloromethane, dichloroethane, toluene, chlorobenzene and a mixture thereof.
- [11] The method of claim 1, wherein a total amount of the organic solvent is 50-800% based on the weight of the total monomer in the monomer solution.
- [12] The method of claim 1, wherein the catalyst mixture comprises a metal catalyst complex composed of the procatalyst and the cocatalyst.
- [13] The method of claim 1, wherein the catalyst mixture is added in a solid phase to the monomer solution.
- [14] The method of claim 1, wherein the amount of the catalyst mixture is such that a molar ratio of the procatalyst to the total monomer is 1:2,500 to 1:200,000.
- [15] The method of claim 1, wherein the monomer solution further comprises a cyclic olefin compound having no polar functional group.
- [16] The method of claim 1, wherein the cyclic olefin polymers having polar functional groups comprise a cyclic olefin homopolymer, a copolymer of cyclic olefin monomers having different polar functional groups, or a copolymer of a cyclic olefin monomer having a polar functional group and a cyclic olefin monomer having no polar functional group.
- [17] The method of claim 1, wherein a weight average molecular weight M_w of the cyclic olefin polymer having a polar functional group is 10,000-1,000,000.
- [18] The method of claim 1, wherein the monomer solution further comprises a linear or branched C_{1-20} olefin.
- [19] A polymer produced using the method of any one of claims 1-18, which is an addition polymer of a cyclic olefin monomer having a polar functional group represented by formula (3) and has a weight average molecular weight M_w of 10,000-1,000,000:



(3)

where m , R_7 , R'_7 , R''_7 and R'''_7 are as defined in claim 3.

- [20] An optical anisotropic film comprising the cyclic olefin polymer having a polar functional group of claim 19.
- [21] The optical anisotropic film of claim 20, which has a retardation value R_{th}

represented by Equation (1) of 70-1000 nm:

$$R_{th} = \Delta(n_y - n_z) \times d$$

(1)

where n_y is a refractive index of an in-plane fast axis measured at 550 nm;

n_z is a refractive index in a direction through the film thickness measured at 550 nm, and

d is a film thickness.

[22]

The optical anisotropic film of claim 21, which is a negative C-plate type optical compensation film for liquid crystal display, satisfying a refractive index requirement of

$$n_x \cong n_y < n_z$$

, in which n_x is a refractive index of an in-plane slow axis, n_y is a refractive index of an in-plane fast axis, and n_z is a refractive index in a direction through the film thickness.